PATENT SPECIFICATION

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(54) IMPROVEMENTS IN CHALCOGENIUM SALTS

(71) We, GENERAL ELECTRIC COMPANY, a corporation organized and existing under the laws of the State of New York, United States of America, of 1 River Road, Schenectady 12305, State of New York, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention relates to improvements in salts which can be used with epoxy resin compositions for curing by exposure to radiant energy.

Epoxy resins have generally been employed in a variety of applications requiring high performance materials. Cure of an epoxy resin can generally be achieved by two package systems based on the incorporation into the resin of active amine containing compounds or carboxylic acid anhydrides. These systems require thorough mixing of the ingredients; in addition, cure time can be several hours.

Another catalyst which can be used to cure epoxy resins as "one package" systems is based on the employment of a Lewis Acid catalyst in the form of an amine complex such as boron trifluoride-monoethylamine. The Lewis Acid is released on heating; cure takes place within 1 to 8 hours and can require a temperature of 160°C and higher. As a result, these one package epoxy compositions cannot be employed to coat heat sensitive devices such as delicate electronic components. Nor can epoxy monomers having low boiling points be used due to the resulting losses to evaporation during cure.

As shown by Schlesinger U.S. Patent 3,703,296, certain photosensitive aromatic diazonium salts can be employed to cure epoxy resins. When photolyzed, these aromatic diazonium salts are capable of releasing, *in situ*, a Lewis Acid catalyst which can initiate the rapid polymerization of the epoxy resin. However, even though these one package epoxy resin mixtures can provide fast curing compositions, a stabilizer must be used to minimise cure in the dark during storage of these mixtures. Despite these measures, gellation of the mixture can occur even in the absence of light. In addition, nitrogen is released during the UV-curve, which can result in film imperfections. Diazonium salts are generally thermally unstable, rendering the use of such materials hazardous because of the possibility of run-away decomposition.

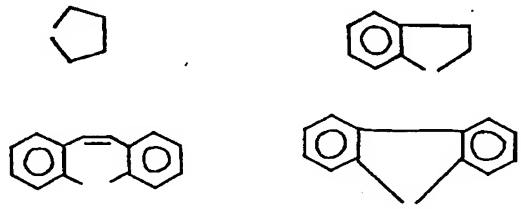
Accordingly the present invention provides a salt for use in curing curable compositions, the salt having the formula

$$(R)_a(R^1)_b(R^2)_cX^+MF_6^-$$

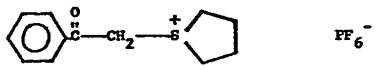
where M is P, As or Sb, R is a monovalent aromatic radical, R^1 is a monovalent alkyl, cycloalkyl or substituted alkyl radical, R^2 is a polyvalent organic aliphatic or aromatic radical forming a heterocyclic or fused ring structure, X is S, Se or Te, a is 0 or a whole number of 1 to 3, b is 0, 1 or 2, c is 0 or 1, where the sum of $a+b+c$ satisfies the valence of X.

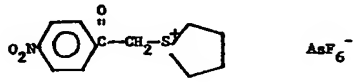
Radicals included by R are, for example, $C_{(6-13)}$ aromatic hydrocarbon radicals such as phenyl, tolyl, naphthyl, anthryl, and such radicals substituted with from 1 to 4 monovalent radicals such as $C_{(1-8)}$ alkoxy, $C_{(1-8)}$ alkyl, nitro, chloro and hydroxy,

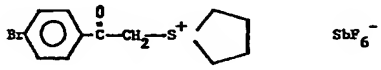
arylacyl radicals such as benzylacyl and phenylacyl, aromatic heterocyclic radicals such as pyridyl and furfuryl. R^1 radicals include $C_{(1-8)}$ alkyl, such as methyl and ethyl, substituted alkyl such as $—C_2H_4OCH_3$, $—CH_2COOC_2H_5$, or $—CH_2COCH_3$. R^2 radicals include such structures as:



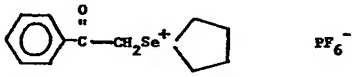
The onium salts included in the formula are for example







and



The salts of this invention can be made by the procedure suitably modified shown in J. W. Knapczyk and W. E. McEwen, J. Am. Chem. Soc., *91* 145, (1969)—A. L. Maycock and G. A. Berchtold, J. Org. Chem. *35*, No. 8, 2532 (1970)—H. M. Pitt, U.S. Patent 2,807,648, E. Goethals and P. De Radzetzky, Bul. Soc. Chim. Belg., *73* 546 (1964)—H. M. Leicester and F. W. Bergstrom, J. Am. Chem. Soc., *51* 3587 (1929).

Thus, the simple starting salts can be prepared according to the procedure of H. M. Leicester and F. W. Bergstrom, J. Am. Chem. Soc., *51* 3587 (1929). The corresponding complex salts, for example, hexafluoroarsenate and hexafluoroantimonate salts can be prepared by adding sodium hexafluoroarsenate or potassium hexafluoroantimonate to an aqueous solution of triphenyl selenorium chloride to produce white crystalline solids which can be dried in vacuo.

The term "epoxy resin" as utilized herein includes any monomeric, dimeric oligomeric or polymeric epoxy material containing a plurality of epoxy functional groups. A monoepoxide can also be used in the composition of this invention either as one or as a mixture with the epoxy resin. For example, those resins which result from the reaction of bisphenol-A (4,4'-isopropylidenediphenol) and epichlorohydrin, or by the reaction of low molecular weight phenol-formaldehyde resins (Novolak resins) with epichlorohydrin, can be used alone or in combination with an epoxy containing compound as a reactive diluent. Such diluents as phenyl glycidyl ether, 4-vinylcyclohexene dioxide, limonene dioxide, 1,2-cyclohexene oxide, glycidyl acrylate, glycidyl methacrylate, styrene oxide and allyl glycidyl ether may be added as viscosity modifying agents.

In addition, the compounds to be cured by the salts can be extended to include polymeric materials containing terminal or pendant epoxy groups. Examples of these compounds are vinyl copolymers containing glycidyl acrylate or methacrylate as one of the comonomers. Other classes of epoxy containing polymers amenable to cure

using the above catalysts are epoxy-siloxane resins, epoxy-polyurethanes and epoxy-polyesters. Such polymers usually have epoxy functional groups at the ends of their chains. Epoxy-siloxane resins and method for making are more particularly shown by E. P. Plueddemann and G. Fanger, J. Am. Chem. Soc. *81* 632—5 (1959). As described in the literature, epoxy resins can also be modified in a number of standard ways such as reactions with amines, carboxylic acids, thiols, phenols and alcohols, as shown in U.S. patents 2,935,488; 3,235,620; 3,369,055; 3,379,653; 3,398,211; 3,403,199; 3,563,850; 3,567,797; 3,677,995; etc. Further examples of epoxy resins which can be used are shown in the Encyclopedia of Polymer Science and Technology, Vol. 6, 1967, Interscience Publishers, New York, pp 209—271.

The curable compositions are further described in our Patent Specification No. 15701/75 (Serial No. 1,516,511) and can be made by blending the epoxy resin, which hereinafter will signify epoxy monomer, epoxy prepolymer, epoxy polymer or mixture thereof, with an effective amount of the Group VIa onium salt or "onium salt". The resulting curable composition which can be in the form of a varnish having a viscosity of from 1 centipoise to 100,000 centipoises at 25°C or a free flowing powder, can be applied to a variety of substrates by conventional means and cured to the tack-free state within 1 second or less to 10 minutes or more.

Depending upon the compatability of the onium salt with the epoxy resin, the Group VIa onium salt can be dissolved or dispersed therein along with an organic solvent such as nitromethane and acetonitrile prior to its incorporation. In instances where the epoxy resin is a solid, incorporation of the onium salt can be achieved by dry milling or by melt mixing the resin whereby the onium salt is incorporated.

It has been found that the onium salt also can be generated *in situ* in the presence of the epoxy resin if desired. For example, an onium salt of the formula,

$$(R)_a(R^1)_b(R^2)_cX^+Q'^-$$

where R, R^1, R^2, X, a, b and c are as previously defined, and Q′ is an anion such as Cl^-, Br^-, I^-, F^-, HSO_4^- and NO_3^- can be separately or simultaneously introduced into the epoxy resin with a Lewis Acid salt of the formula

$$M'(MF_d)$$

where M′ is a metal cation, such as Na^+, K^+, Ca^{++}, Mg^{++}, Fe^{++}, Ni^{++}, Co^{++} and Zn^{++} and organic cations such as ammonium or pyridinium, and where M is defined in formula I above.

Experience has shown that the proportion of onium salt to epoxy resin can vary widely inasmuch as the salt is substantially inert, unless activated. Effective results can be achieved if a proportion of from .1% to 15% by weight of onium salt is employed, based on the weight of curable composition.

The curable compositions may contain inactive ingredients such as inorganic fillers, dyes, pigments, extenders, viscosity control agents, process aids and UV-screens in amounts of up to 100 parts of filler per 100 parts of epoxy resin. The curable compositions can be applied to such substrates as metal, rubber, plastic, molded parts or films, paper, wood, glass cloth, concrete and ceramic.

Some of the applications in which the curable compositions of the present invention can be used are, for example, protective, decorative and insulating coatings, potting compounds, printing inks, sealants, adhesives, photoresists, wire insulation, textile coatings, laminates, impregnated tapes and printing plates.

Cure of the curable composition can be achieved by activating the onium salt to provide the release of the Lewis Acid catalyst. Activation of the onium salt can be achieved by heating the composition at a temperature in the range of from 150°C to 250°C. Preferably cure can be achieved by exposing the curable composition to radiant energy such as electron beam or ultraviolet light.

In order that those skilled in the art will be better able to practice the invention, the following examples are given by way of illustration and not by way of limitation. All parts are by weight.

EXAMPLES 1 and 2

Triphenylselenonium chloride was prepared according to the procedure of H. M. Leicester and F. W. Bergstrom, J. Am. Chem. Soc. *51* 3587 (1929) starting with diphenyl selenide. The corresponding hexafluoroarsenate and hexafluoroantimonate salts were prepared by adding sodium hexafluoroarsenate, or potassium hexafluoro-

antimonate to an aqueous solution of triphenylselenonium chloride. The products were white crystalline solids which were dried in vacuo.

Three percent solutions of the above salts in 4-vinylcyclohexene dioxide were cured as 2 mil films at a distance of six inches from a GE H3T7 lamp. The following cure times were observed:

Example	Salt	Cure Time
1	$(C_6H_5)_3Se^+AsF_6^-$	10 sec.
2	$(C_6H_5)_3Se^+SbF_6^-$	3 sec.

EXAMPLE 3

There were added 6 parts of a 50% aqueous solution of triphenylsulfonium chloride and 2.1 parts of $NaAsF_6$ to 97 parts of an 80:20 mixture of bisphenol-A-diglycidyl ether and 4-vinylcyclohexene dioxide. The reaction mixture was agitated by stirring for one-half hour and then allowed to settle. An aliquot of the resin was taken and spread onto a glass plate using a draw knife with a 3 ml aperture. A tack-free film formed within 15 seconds after exposure to an H3T7 lamp at a distance of six inches. The film was hard and clear.

Resistors were potted in the above resin by dipping the resistor into the sensitized resin and then curing it by rotating the resistor for 30 seconds beneath the ultraviolet lamp.

EXAMPLE 4

There were added 2.6 parts phenacyltetramethylene sulfonium bromide to a mixture of 95 parts of 4-vinylcyclohexene dioxide containing 2.2 parts of $NaAsF_6$. The solution was placed in a dark bottle and rolled on a ball mill for 8 hours. After the salts were removed by filtration, the solution was coated onto a 3 in×6 in steel panel and cured by exposure to the ultraviolet radiation of a H3T7 lamp at a distance of 2 inches. A hard coating was obtained after 15 seconds exposure which could not be removed by rubbing the coating with acetone.

EXAMPLE 5

There were added with stirring 89 parts of aluminium chloride in small portions to a solution of 122 parts of 2,6-xylenol in 505.12 parts of carbon disulfide maintained at 10°C. To the resulting greenish solution were added 79.5 parts of thionyl chloride in a dropwise fashion maintaining the temperature between 10 and 15°C. A black precipitate and solution was obtained which was stirred for an additional 2 hours and then poured onto 1000 parts of ice containing about 50 parts of concentrated HCl. This mixture was placed on a steam bath to remove CS_2 and to decompose the complex. A tan solid was obtained which was filtered, washed with water and dried.

To a solution of 21.5 parts of the above crude product in about 117 parts of hot absolute ethanol were added 11.4 parts of $KAsF_6$ and 10 parts of water. The reaction mixture was stirred and more water was added to effect the precipitation of product. The product was filtered, washed with water and dried. A material was obtained having a m.p. of 245—251°C. Based on method of preparation and elemental analysis for $C_{24}H_{27}O_2SAsF_6$. Calc. %C, 49.3; %H, 4.62; %S, 5.48. Found: %C, 49.4; %H, 4.59; %S, 5.55, the product was tris-3,5-dimethyl-4-hydroxy-phenyl sulfonium hexafluoroarsenate.

A three percent solution of the above onium salt was made with 4-vinylcyclohexene dioxide. Cure of the solution was effected by irradiating a 2 mil film on glass according to the procedure described in Example 1. A hard mar-resistant coating was obtained after 5 seconds of irradiation.

WHAT WE CLAIM IS:—

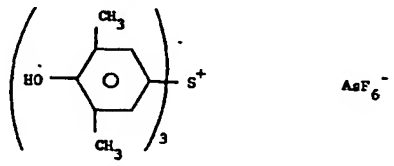
1. A salt of the formula:

$$(R)_a(R^1)_b(R^2)_cX^+MF_6^-$$

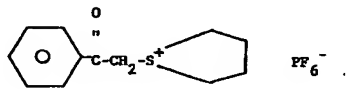
where M is P, As or Sb, R is a monovalent aromatic radical, R^1 is a monovalent alkyl, cycloalkyl or substituted alkyl radical, R^2 is a polyvalent organic aliphatic or aromatic radical forming a heterocyclic or fused ring structure, X is S, Se or Te, a is 0 or a whole number of 1 to 3, b is 0, 1 or 2, c is 0 or 1, where the sum of $a+b+c$ satisfies the valence of X.

2. A salt as claimed in claim 1 wherein X is S.

3. A salt as claimed in claim 1 of the formula:



4. A salt as claimed in claim 1 of the formula:



5. A salt as claimed in claim 1 substantially as hereinbefore described in any one of Examples 1 to 5.

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